from Cromer and Waber[33] for Sm and C. The scattering for Sm was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[34] The final fractional coordinates are given in Table III. The final values of the thermal parameters are given in the supplementary material.

Acknowledgment. For support of this research we thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (W.J.E., I.B.), the National Science Foundation (J.L.A., W.E.H.), and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar grant (W.J.E).

Registry No. I, 84642-15-9; II, 84642-16-0; $LiC{\equiv}CC(CH_3)_3$, 37892-71-0; $(CH_3C_5H_4)_2SmCl(THF)$, 84623-27-8; $HP(C_6H_5)_2$, 829-85-6; $HC{\equiv}CC(CH_3)_3$, 917-92-0; $SmCl_3$, 10361-82-7; $CH_3C_5H_4Na$, 55562-83-9; THF, 109-99-9.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters, and complete bond length and angle information (12 pages). Ordering information is given on any current masthead page.

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Structure of the Hydrogenation Catalyst $[(\widehat{P\ P})Rh(NBD)]ClO_4$, $\widehat{P\ P} = (\eta^5\text{-}[(CH_3)_3C]_2PC_5H_4)_2Fe$, and Some Comparative Rate Studies

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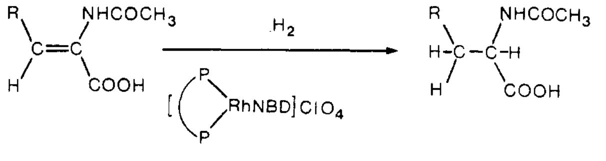
Received September 14, 1982

The structure of the hydrogenation catalyst precursor $[(\widehat{P\ P})Rh(NBD)]ClO_4$ [$\widehat{P\ P} = (\eta^5\text{-}[(CH_3)_3C]_2PC_5H_4)_2Fe$; NBD = norbornadiene] has been determined. The cationic moiety finds Rh in a very distorted "square-planar" environment coordinated to the double bonds of the norbornadiene ligand at distances of 2.181 (5) and 2.161 (5) Å and the phosphorus atoms of the bidentate chelating phosphine ligand at distances of 2.466 (1) and 2.458 (1) Å. Relative rate studies, employing the aforementioned catalyst precursor and also the related precursor where $\widehat{P\ P} = (\eta^5\text{-}[(C_6H_5)_2PC_5H_4]_2Fe)$, have been performed for the hydrogenation reactions of (acylamino)acrylic, (acylamino)cinnamic, itaconic, and methylcinnamic acids in methanol and/or ethanol. The results of these experiments, together with related work previously reported, are discussed and rationalized in terms of the steric and electronic effects exerted by the substituents attached to the chelating bis(phosphine) ligands.

Most studies of homogeneous catalysis by metal complexes have used tertiary phosphines such as triphenylphosphine or bis(tertiary phosphines) such as 1,2-bis(diphenylphosphino)ethane as ligands. With appropriate synthetic ingenuity similar optically active ligands can be isolated as one or the other enantiomer and complexes of these have been studied with respect to their ability to catalyze asymmetric reactions. In particular notable success has been achieved in the asymmetric hydrogenation of amino acid precursors such as α-(acylamino)cinnamic acid using cationic rhodium(I) complexes of optically active chelating bis(tertiary phosphines) as catalyst precursors:[1] for example, eq 1, R = C_6H_5 and $\widehat{P\ P}$ = $(C_6H_5)_2PCH(CH_3)CH(CH_3)P(C_6H_5)_2$, chiraphos, where the optical yield is nearly 100%.[2]



(1)

The almost universal use of ligands with arylphosphorus moieties in reaction such as (1) has resulted in much attention being focused on the aryl rings with respect to their involvement in the discrimination step. Thus heavy emphasis has been placed on the idea that the incoming prochiral substrate "sees" a chiral array of aryl rings (propellors) held by a fixed complex-ring conformation.[3,4] Binding of one face or the other of the substrate gives a pair of diastereomeric intermediates in equilibrium that are hydrogenated at different rates to afford the mixture of enantiomeric products. These ideas have been elegantly elaborated by the groups of Halpern and Bosnich and co-workers,[4-7] who also point out that the rate or hydrogenation of the diastereomers 1 will be governed by the stability of the *cis*-dihydride intermediate **2**: see eq 2 where $\widehat{P\ P}$ is optically active and $\widehat{=\ O}$ (where O is gen-

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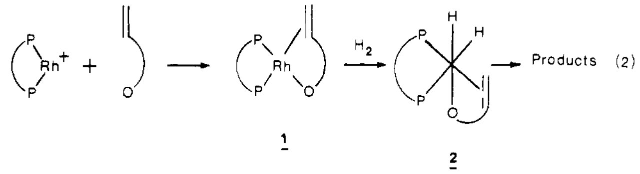
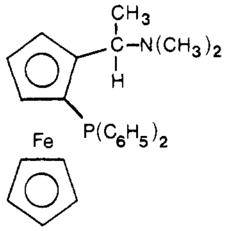
erally believed to be the *N*-acyl oxygen atom[8]) is used to symbolize the type of substrate shown in eq 1.

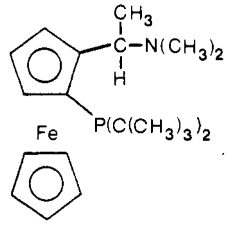


There are eight possible octahedral isomers of 2, four for each diastereomer.[4] The thesis is advanced that the more stable the intermediate(s) 2 is the faster it will be formed and thus any further reaction to give product will be channelled through this intermediate. Again the dissymmetric array of aryl groups on the ligand has been invoked as a contributor to the stability of 2.[4]

In this connection it should be noted that the cationic rhodium complexes of optically active 3, PPFA, give high optical yields in reactions such as (1) and that the correct product stereochemistry can be predicted from considerations of models of six-coordinate intermediate like 2 (P$\frown$P = 3 with both P and N bound to rhodium[9]). However, the ligand contains only two phenyl rings, the bare minimum for a chiral array. In order to test this result further, we prepared rhodium complexes of 4 and found them to be good asymmetric hydrogenation catalysts. In some cases the change to the bulky *tert*-butyl group resulted in faster reaction rates and higher optical yields.[10] Only a limited amount of other data is available on asymmetric reactions catalyzed by complexes of alkylphosphines[11,12] although induction is observed.



3, PPFA



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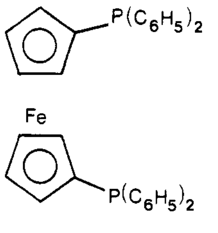

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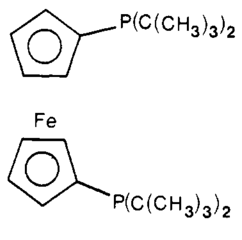

6 DB^{t}PF

In view of these results it is important to garner further information about the structures of metal complexes of bis(tertiary phosphines) with alkylphosphorus moieties and try to determine what effect these moieties have on reaction rates. This paper addresses both these issues and describes some relative rate studies of catalytic hydrogenation using rhodium complexes of 5 and 6 together with the structure of a catalyst precursor containing 6.

Table I. Crystal Data for $C_{33}H_{52}ClFeO_4P_2Rh$

space group	$P2_1/n$	M_r	768.933
a, Å	8.599 (2)	μ, cm^{-1}	11.34
b, Å	23.360 (11)	ρ_{obsd},^{a} g mL^{-1}	1.53
c, Å	16.616 (5)	ρ_{calcd}, g mL^{-1}	1.534
β, deg	94.04 (2)	final R_1^{b}	0.031
U, Å^3	3329.4	final R_2^{c}	0.037

^{a} Flotation in a CH_2Cl_2/CH_2I_2 mixture. ^{b} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Experimental Section

Air-sensitive reagents and products were manipulated in a nitrogen atmosphere using Schlenk techniques. Solvents were purified and dried by standard techniques.

^{1}H NMR spectra were recorded on either a Varian XL100 spectrometer at 100 MHz or a Bruker WM 400 spectrometer at 400 MHz. 1,1′-Bis(diphenylphosphino)ferrocene was prepared by the literature method.[13] Hydrogenation reactions were carried out using a gas-uptake apparatus as described by James and co-workers.[14]

Microanalyses were performed by Mr. P. Borda of the Chemistry Department, University of British Columbia.

Preparation of 1,1′-Bis(di-*tert*-butylphosphino)ferrocene (6). 1,1′-Dilithioferrocene–bis(*N,N,N′,N′*-tetramethylethylenediamine) (7.5 g, 23.9 mmol), isolated according to the literature method,[13] was suspended in freshly distilled *n*-hexane (40 mL). To this suspension, maintained at −78 °C, was added chlorodi-*tert*-butylphosphine (8.7 g, 48.2 mmol).[15] The mixture was allowed to warm to room temperature and was stirred for 2 h. Following hydrolysis with water (20 mL), the hexane layer was separated, dried over $MgSO_4$, filtered, and reduced in volume to 10 mL. This oily solution was then chromatographed on alumina. Removal of solvent from the resulting deep orange solution (the second band that eluted with a mixture of petroleum ether and diethyl ether, 30/70) afforded a dark oily product (4.5 g). The product was not purified further. (Careful chromatography was required to separate the product from a white phosphine byproduct which eluted with petroleum ether). ^{1}H NMR: δ 4.20–4.50 (m, 8), 1.22 (d, 36, J_{P-H} = 11 Hz).

Preparation of [(P$\frown$P)Rh(NBD)]ClO$_4$(P$\frown$P = 6). The title complex was prepared essentially using the procedure of Schrock and Osborne[16] with minor modification.

The THF solution (2 mL) of $NaClO_4$ (189.47 mg, 1.55 mmol) was added to a solution of $[(NBD)RhCl]_2$ (356.60 mg, 0.77 mmol) and 6 (1.1 g, 2.32 mmol) in benzene (2 mL). The mixture was allowed to stir for 2 days at room temperature after which time solvents were removed to leave a reddish brown solid. This was washed with diethyl ether (20 mL), dissolved in dichloromethane (2 mL), and filtered through a Schlenk filter. To the filtrate was added a 3:2 mixture of diethyl ether and ethanol (5 mL), and the solution was cooled at 0 °C to give deep red crystals. Large crystals were grown by dissolving the crystals in dichloromethane (1 mL) and allowing cyclohexane (4 mL) to diffuse slowly into the dichloromethane layer: yield 80%, not optimized; decomp pt 153–155 °C; ^{1}H NMR δ 1.63 (d, 36, *t*-Bu groups), 2.80 (b s, 2, NBD, C_7C_8), 3.05 (m, 2, NBD, C_3C_6), 4.58 (dd, 8, ferrocenyl), 5.33 (m, 4, NBD, $C_1C_2C_4C_5$, J_{P-H} = 12 Hz). Anal. Calcd for $C_{33}H_{52}ClFeO_4P_2Rh$: C, 51.55; H. 6.77. Found: C, 51.46; H, 6.70.

Structure Determination of [(P$\frown$P)Rh(NBD)]$^+$[ClO$_4$]$^-$ (P$\frown$P = 6). A deep red crystal 0.06 × 0.11 × 0.13 mm was mounted in a Lindemann glass tube. Precession and Weissenberg photographs were used to obtain approximate unit-cell dimensions and to uniquely define the space group as $P2_1/n$, which is a nonstandard setting of the space group $P2_1/c$ (systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$). Accurate cell dimensions

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Table II. Final Positional and Thermal Parameters for $[(DB\,^{t}PF)Rh(NBD)]^{+}[ClO_4]^{-}$

atom	x	y	z	B_{eq},[a] Å^2
Rh	0.32702 (4)	0.173 832 (15)	0.243 302 (20)	2.155 (13)
Fe	0.06095 (7)	0.013 41 (3)	0.278 30 (4)	2.66 (3)
P(1)	0.19211 (12)	0.112 59 (5)	0.139 56 (6)	1.95 (5)
P(2)	0.27014 (14)	0.127 79 (5)	0.370 98 (7)	2.42 (5)
Cl	0.02521 (17)	0.627 72 (6)	0.719 49 (10)	5.23 (9)
O(1)	0.0333 (6)	0.679 47 (22)	0.762 6 (4)	10.2 (5)
O(2)	0.1264 (6)	0.630 45 (31)	0.660 0 (3)	10.4 (5)
O(3)	0.0749 (8)	0.582 46 (27)	0.770 1 (4)	11.4 (5)
O(4)	−0.1277 (5)	0.618 12 (25)	0.686 3 (5)	11.8 (7)
C(1)	0.0501 (5)	0.146 85 (20)	0.059 70 (25)	2.52 (21)
C(11)	−0.0484 (6)	0.189 75 (22)	0.103 58 (31)	3.83 (27)
C(12)	0.1290 (6)	0.177 89 (25)	−0.007 13 (30)	4.24 (29)
C(13)	−0.0622 (6)	0.102 85 (24)	0.017 76 (29)	3.98 (30)
C(2)	0.3529 (5)	0.074 77 (20)	0.088 24 (26)	2.63 (22)
C(21)	0.4726 (6)	0.115 93 (23)	0.056 94 (31)	3.81 (27)
C(22)	0.2928 (6)	0.036 85 (22)	0.016 43 (28)	3.47 (25)
C(23)	0.4412 (5)	0.038 27 (22)	0.153 60 (29)	3.44 (26)
C(3)	0.1150 (5)	0.175 70 (21)	0.412 65 (26)	3.15 (23)
C(31)	−0.0271 (6)	0.173 69 (23)	0.352 61 (32)	4.04 (26)
C(32)	0.1685 (6)	0.238 47 (23)	0.416 77 (31)	4.23 (30)
C(33)	0.0688 (7)	0.158 77 (25)	0.497 58 (32)	5.39 (40)
C(4)	0.4351 (6)	0.113 59 (21)	0.454 65 (29)	3.60 (27)
C(41)	0.5732 (6)	0.089 83 (25)	0.412 69 (36)	4.71 (32)
C(42)	0.3856 (7)	0.069 03 (24)	0.515 85 (31)	4.62 (33)
C(43)	0.4846 (8)	0.166 77 (26)	0.503 88 (38)	6.13 (40)
C(51)	0.0664 (5)	0.054 71 (18)	0.171 10 (25)	2.27 (20)
C(52)	−0.0790 (5)	0.065 14 (22)	0.207 23 (28)	3.18 (26)
C(53)	−0.1530 (6)	0.011 32 (27)	0.216 61 (31)	4.35 (34)
C(54)	−0.0598 (6)	−0.031 40 (22)	0.188 04 (31)	4.04 (28)
C(55)	0.0745 (5)	−0.006 39 (20)	0.160 13 (27)	3.07 (24)
C(61)	0.1878 (5)	0.055 60 (19)	0.367 04 (25)	2.60 (22)
C(62)	0.2724 (5)	0.007 41 (21)	0.338 63 (26)	3.08 (24)
C(63)	0.1872 (6)	−0.042 85 (21)	0.350 75 (31)	3.94 (29)
C(64)	0.0506 (7)	−0.027 93 (23)	0.386 32 (30)	4.44 (32)
C(65)	0.0503 (6)	0.032 03 (22)	0.397 46 (27)	3.64 (27)
C(71)	0.3937 (6)	0.233 95 (21)	0.150 96 (28)	3.39 (26)
C(72)	0.5614 (5)	0.207 24 (24)	0.258 82 (35)	4.22 (32)
C(73)	0.5609 (6)	0.243 83 (23)	0.182 90 (32)	4.00 (28)
C(74)	0.5523 (6)	0.303 92 (23)	0.218 47 (33)	4.46 (29)
C(75)	0.4119 (6)	0.289 28 (22)	0.267 55 (31)	4.00 (28)
C(76)	0.4711 (6)	0.235 19 (23)	0.311 32 (30)	3.78 (27)
C(77)	0.3017 (6)	0.262 16 (21)	0.203 02 (31)	3.40 (25)

[a] $B_{eq} = 8\pi^2(U_{11}^2 + U_{22}^2 + U_{33}^2)^{1/2}$.

(Table I) were determined by least-squares refinement of the diffractometer angles of 20 independent reflections (2θ = 28–38°; λ (Mo Kα_1) = 0.709 26 Å) chosen from a variety of points in reciprocal space. Data were collected, at 293 K, by using a Picker FACS-I four-circle diffractometer with a graphite monochromator and a scintillation detector with pulse height discrimination. The takeoff angle was 3° and symmetrical θ–2θ scans (2° min^{-1}) of (1.2 + 0.692 tan θ)° were used. Stationary-crystal–stationary-counter counts of 10% of the scan time were taken at each side of the scan. A peak profile analysis was performed on each reflection, and the intensity and its associated error were determined by the method of Grant and Gabe.[17] Measurement of two standards every 70 reflections showed there to be a slight variation in intensity that was corrected appropriately.

Intensities were measured for 5248 independent reflections ($2\theta \le 48°$), of which 3531 were classed observed [$I \ge 2.3\sigma(I)$]. Lorentz–polarization corrections and absorption corrections were made (transmission coefficients varied from 0.782 to 0.874).

Determination and Refinement of the Structure. The structure was solved by Patterson and Fourier methods. After location and refinement of the non-hydrogen atoms of the molecule a difference Fourier synthesis utilizing a limited data set ($2\theta \le 30°$) revealed the majority of hydrogen atoms; those hydrogen atoms not located, we believe, would have appeared in a subsequent difference Fourier synthesis; however, for the sake of convenience their positions were calculated. Block-diagonal least-squares refinement of the coordinates of all the atoms of the molecule with variable anisotropic temperature factors for non-hydrogen atoms and fixed isotropic temperature factors (B_{eq} = 6.0 Å^2) for hydrogen atoms gave final agreement factors of R_1 = 0.031 and R_2 = 0.037 for 535 variables. The final difference map was flat apart from one peak 0.35 (6) e/Å^3 in the vicinity of the perchlorate anion. Analysis of the data set as a function of $|F_o|$ and sin θ led to a weighting scheme employing weights of the form $w = 1/(\sigma(F^2) + 0.0004F^2)$. Atomic scattering factors including anomalous dispersion were taken from ref 18. Final positional parameters and B_{eq} temperature factors are given in Table II. The computer programs used here are those belonging to "the PDP-8e crystal structure system".[19]

Results and Discussion

Description of Structure. The structure and numbering scheme of the $[(P^\frown P)Rh(NBD)]^+$ cation, $P^\frown P$ = **6**, is shown in Figure 1, while a stereoview is shown in Figure 2. Bond distances and angles are given in Table III. The cation has an approximate twofold axis along the Fe···Rh direction. With the assumption that the double bonds of the norbornadiene (NBD) ligand occupy single coordination sites, the Rh atom may be described, very crudely, as lying in a square-planar environment. The angles within the (NBD)RhP$_2$ "plane" range from 68.4° for MP(1)–Rh–

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Table III. Selected[a] Interatomic Distances (Å) and Angles (deg) for $[(DB^tPF)Rh(NBD)]^+[ClO_4]^-$

Bond Distances

Rh-P(1)	2.466 (1)	Rh-P(2)	2.458 (1)	P(1)-C(1)	1.914 (4)	P(2)-C(3)	1.908 (5)
Rh-C(71)	2.186 (5)	Rh-C(76)	2.161 (5)	P(1)-C(2)	1.893 (4)	P(2)-C(4)	1.943 (5)
Rh-C(72)	2.160 (5)	Rh-C(77)	2.175 (5)	P(1)-C(51)	1.831 (4)	P(2)-C(61)	1.828 (5)
Fe-C(51)	2.029 (4)	Fe-C(61)	2.027 (4)	C(71)-C(73)	1.514 (7)	C(76)-C(75)	1.527 (8)
Fe-C(52)	2.025 (5)	Fe-C(62)	2.019 (4)	C(72)-C(73)	1.524 (8)	C(77)-C(75)	1.518 (7)
Fe-C(53)	2.042 (5)	Fe-C(63)	2.042 (5)	C(73)-C(74)	1.527 (8)	C(75)-C(74)	1.542 (7)
Fe-C(54)	2.050 (5)	Fe-C(64)	2.046 (5)	C(71)-C(77)	1.380 (7)	C(72)-C(76)	1.373 (8)
Fe-C(55)	2.029 (5)	Fe-C(65)	2.036 (5)	av C-C(*t*-Bu)	1.534 (3)	av C-C(Cp)	1.418 (6)[d]

Bond Angles

P(1)-Rh-P(2)	103.71 (5)	MP(1)-Rh-MP(2)	68.4	C(1)-P(1)-C(2)	109.5 (2)	C(3)-P(2)-C(4)	109.5 (2)
P(1)-Rh-MP(1)[b]	99.7	P(2)-Rh-MP(1)	148.9	C(1)-P(1)-C(51)	98.4 (2)	C(3)-P(2)-C(61)	106.0 (2)
P(1)-Rh-MP(2)	150.9	P(2)-Rh-MP(2)	98.4	C(2)-P(1)-C(51)	104.4 (2)	C(4)-P(2)-C(61)	97.5 (2)
Rh-P(1)-C(1)	119.2 (2)	Rh-P(2)-C(3)	104.1 (2)	P(1)-C(51)-C(52)	122.7 (3)	P(2)-C(61)-C(62)	122.0 (3)
Rh-P(1)-C(2)	105.3 (1)	Rh-P(2)-C(4)	120.8 (2)	P(1)-C(51)-C(55)	131.3 (3)	P(2)-C(61)-C(65)	132.2 (4)
Rh-P(1)-C(51)	119.1 (1)	Rh-P(2)-C(61)	118.2 (1)	Cp(1)-Fe-Cp(2)[c]	177.2		

[a] Further bond parameters have been deposited. [b] MP(1) is the midpoint between C(71) and C(77); MP(2) is the midpoint between C(72) and C(76). [c] Cp(1) is the centroid of C(51)-C(55); Cp(2) is the centroid of C(61)-C(65). [d] There is some indication of localization which would invalidate this 'average'. See supplementary material.

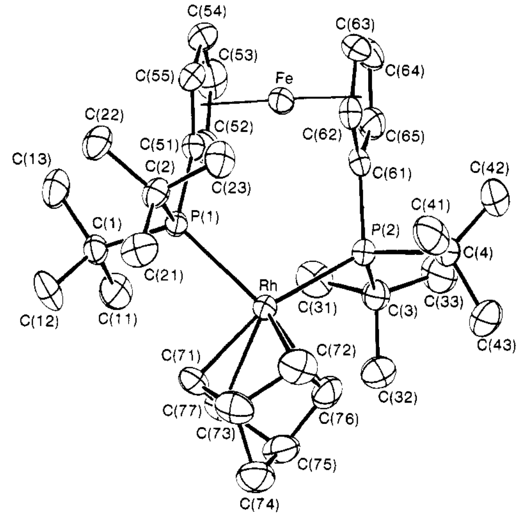
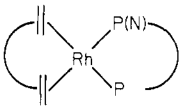


Figure 1. ORTEP diagram and numbering scheme for the $[(\eta^5\text{-}[(CH_3)_3C]_2P(C_5H_4)_2Fe)Rh(NBD)]$ cation. Atoms are represented by 50% probability thermal ellipsoids. (Hydrogen atoms have been omitted for clarity.)

Table IV. Comparison of Rh Coordination Spheres of the Type



bond parameter[a, b]	[(PPFA)-Rh(NBD)]$^+$	[((*S,S*)-chiraphos)-Rh(COD)]$^{+c}$	present compd
Rh-P	2.28 (1)	2.275 (1), 2.266 (1)	2.466 (1), 2.458 (1)
Rh-N	2.26 (3)		
Rh-MP	2.00, 2.14	2.137, 2.138	2.069, 2.048
P-Rh-P(N)	95 (1)	83.82 (6)	103.71 (5)
MP(1)-Rh-MP(2)	71	85.2	68.4
P(N)-Rh-MP	165	173.8	148.9
"diagonals"	170	173.9	150.9

[a] MP denotes the central point along the line joining two carbons of a double bond. [b] Distances are in angstroms and angles in degrees. [c] Determined in this laboratory; from data presented in ref 5.

MP(2) to 103.72 (5)° for P(1)-Rh-P(2), whereas the angles across the "diagonals" are 148.9 and 150.9°, respectively, for P(2)-Rh-MP(1) and P(1)-Rh-MP(2). [MP(1) is the midpoint between C(71) and C(77); MP(2) is the midpoint between C(72) and C(76).] This coordination sphere is far more distorted than observed in comparable compounds,[9,20,21] e.g., P⌒P = 3[4] and chiraphos[20] (Table IV). The extreme distortion found in the present compound is in our opinion the result of steric repulsion between the NBD ligand and the *tert*-butyl substituents on the chelating phosphine ligand. In fact the "bite" of the NBD ligand (as defined by the "MP(1)RhMP(2)" plane) is twisted by 36.8° with respect to the "P(1)RhP(2)" plane. Evidence for steric repulsion is afforded by the short intramolecular H···H distances of 2.09 Å for H(76A)-H(43C) and 2.07 Å for H(71A)-H(12A).

The Rh-P distances of 2.466 (1) and 2.458 (1) Å found here are significantly longer than found in related compounds (Table IV). This observation is undoubtedly the result of steric crowding at the Rh atom caused by the bulky *tert*-butyl substituents joined to the phosphorus atom. Similar phenomena, for a variety of transition-metal complexes, have been cited by Tolman.[22]

The P-Rh-P angle of 103.71 (5)° found here is larger than found in related compounds (Table IV). In the case of [((*S,S*)-chiraphos)Rh(COD)]$^+$ the very small P-Rh-P angle of 83.82 (6)° is typical of a five-membered chelating phosphine ligand.[20,23,24] Furthermore, the P-Rh-N angle of 95 (1)° found when P⌒P = 3 does not appear unusual when one considers it is contained within a six-membered chelating ring. The P-Rh-P angles in other related cations where P⌒P is $(C_6H_5)_2PCH(CH_3)CH_2CH(CH_3)P(C_6H_5)_2$, (*S,S*)-skewphos, or $(C_6H_5)_2PCH(CH_3)_3CH_2CH_2P(C_6H_5)_2$, (*S*)-chiraphos, are 94.67° and 94.12°, respectively.[25] However, the value for P-Rh-P determined in this work seems especially large and can, again, be attributed to steric crowding at the Rh atom. Explanation of the angle in this way rather than, in terms of the ferrocenyl moiety, "fixing" the angle at this value seems more appropriate when one considers that atoms P(1) and P(2) are 0.154 (1) and 0.164 (1) Å, respectively, out of the planes defined by their respective Cp rings (in a direction away from the Rh atom);

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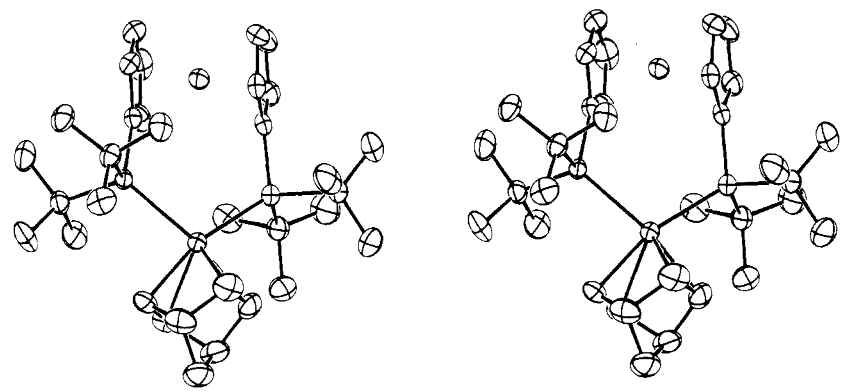
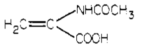
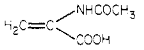
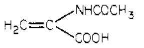
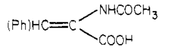
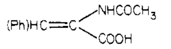
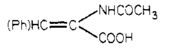
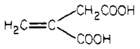
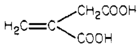
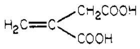
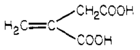
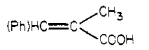
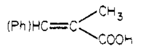


Figure 2. Stereoview of the $[(\eta^5\text{-}[(CH_3)_3C]_2P(C_5H_4)_2Fe)Rh(NBD)]^+$ cation. Atoms are represented by 50% probability thermal ellipsoids. (Hydrogen atoms have been omitted for clarity.)

Table V. Hydrogenation of Olefins Catalyzed by Cationic Rhdoium(I) Complexes $[(\text{P͡P})RhNBD]^+ClO_4^{-\,a}$

P͡P	olefin	solvent	T_{induc}, s	T_∞, s	max rate, mol s^{-1}
5	 $H_2C=C(NHCOCH_3)COOH$	C_2H_5OH	8 ± 2	60 ± 5	5.9×10^{-6}
6	 $H_2C=C(NHCOCH_3)COOH$	C_2H_5OH	27 ± 1	700 ± 25	3.2×10^{-7}
6	 $H_2C=C(NHCOCH_3)COOH$	CH_3OH	17 ± 1	375 ± 25	7.1×10^{-7}
5	 $(Ph)HC=C(NHCOCH_3)COOH$	C_2H_5OH	8 ± 2	150 ± 20	3.4×10^{-6}
6	 $(Ph)HC=C(NHCOCH_3)COOH$	C_2H_5OH	30 ± 2	1780 ± 20	1.4×10^{-7}
6	 $(Ph)HC=C(NHCOCH_3)COOH$	CH_3OH	18 ± 2	680 ± 20	2.9×10^{-7}
5	 $H_2C=C(CH_2COOH)COOH$	C_2H_5OH	8 ± 2	180 ± 5	1.8×10^{-6}
5	 $H_2C=C(CH_2COOH)COOH$	CH_3OH	8 ± 2	125 ± 5	2.8×10^{-6}
6	 $H_2C=C(CH_2COOH)COOH$	C_2H_5OH	9 ± 2	90 ± 5	4.1×10^{-6}
6	 $H_2C=C(CH_2COOH)COOH$	CH_3OH	8 ± 2	200 ± 15	5.5×10^{-6}
5	 $(Ph)HC=C(CH_3)COOH$	C_2H_5OH	0	0	0
6	 $(Ph)HC=C(CH_3)COOH$	C_2H_5OH		600 ± 20	5.5×10^{-7}

[a] Apart from one all reactions are stoichiometric. [substrate] = 2.00×10^{-2} M in 10 mL of solvent; [catalyst] = 2.00×10^{-4} M; $p(H_2) = 1$ atm; $t = 30$ °C; T_∞ = time to complete 100% uptake of H_2; T_{induc} = induction time before measurable H_2 uptake; max rate = maximum slope of gas-uptake plot.

cf. the related free ligand 3 that has its substituted P atom displaced 0.06 (1) Å above the plane of its Cp ring.[26]

Although we do not yet have data for the corresponding derivatives of 5, the following values for P–M–P angles in other complexes of 5 are relevant:[27] (P͡P)Mo(CO)$_4$, 95.3°; (P͡P)PdCl$_2$, 98.0°; (P͡P)NiBr$_2$, 102.5°. In the nickel complex the coordination is pseudotetrahedral yet the P–metal–P angle is still less than for the square-planar rhodium complex of 6.

The Rh–C distances of 2.186 (5) and 2.175 (5) Å for one double bond and 2.161 (15) and 2.160 (5) Å for the second double bond are similar to values reported in related compounds.[6,17,25,26] The average Rh–C distances to each double bond are 2.181 (5) and 2.161 (5) Å, suggesting perhaps a slight asymmetry in the binding of the NBD ligand to the Rh atom; however, the esd's on these values are too large to be certain. The very small MP(1)–Rh–MP(2) angle of 68.4°, similar to the value of 71° observed when P͡P = 3,[4] is imposed on the structure by the rigidity of the NBD ligand.

The bond parameters of the NBD ligand are similar to those found in other coordinated NBD ligands.[9,30] The coordinated C=C double bonds (1.380 (7) and 1.373 (8) Å) are as expected[30a] significantly larger than the recognized value of 1.335 (5) Å for the uncoordinated ligand.[31]

The conformational arrangement of the *tert*-butyl groups appears to be governed by steric interaction of CH_3 substituents of the phosphine ligand with other CH_3 substituents, the Cp rings, and the NBD ligand; e.g., H(33A)–H(43B) = 2.15 Å, H(11A)–H(52A) = 1.91 Å, and H(43C)–H(76A) = 2.09 Å (further nonbonded H···H con-

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tacts have been deposited as supplementary data).

Hydrogenation Studies. The results of a number of hydrogenation reactions using the catalyst precursors $[(\widehat{P\ P})RhNBD]^+ClO_4^-$, $\widehat{P\ P}$ = **5** or **6**, are listed in Table V. Generally all the gas-uptake plots under the chosen conditions show a short induction period followed by an almost linear region corresponding with the maximum rate. Rates of the order of 6×10^{-6} mol s^{-1} are about the maximum we can measure by using the manual gas-uptake system; however, there can be no doubt about the trends. Thus the results for the (acylamino)cinnamic and (acylamino)acrylic acids reveal that the rates obtained with the tetraphenyl derivative **5** are greater than those obtained with **6**. The rate difference is marginal for itaconic acid with a reversal of order. The trend is continued with methylcinnamic acid where the derivative of **5** is not catalitically active.[32] The rate in methanol seem to be greater than in ethanol although some caution is necessary as the rate of solution of the catalyst in the alcohol could be a factor.

All the reactions proceed very quickly, and the rates are very much faster than we have observed with cationic rhodium complexes of **3** and **4**.[10] Here again the presence of phenyl groups can result in slower reactions. For example, itaconic acid (5×10^{-2} M) is only 21% hydrogenated in 72 h by using a catalyst derived from **3** yet is 100% hydrogenated in 16 h by using one derived from **4**[10] ([catalyst] = 0.01 [substrate] as in the present study).

When hydrogen is added to solution of $[(\widehat{P\ P})RhNBD]^+ClO_4^-$ ($\widehat{P\ P}$ = **5** or **6**), there is a color change from yellow to red in MeOH-d_4. The ^1H NMR spectra show that norbornane is present. Brown and co-workers[34] have shown no hydride is formed by using similar chelating phosphines. However, this does not preclude their existence in this reaction. Work is being carried out at present in a variety of solvents to elucidate the mechanistic details. The mechanism of the reaction is probably as depicted by eq 2 with the rate-determining step being the cis addition of hydrogen to the four-coordinate intermediate. In the event that the substrate does not chelate the vacant site would be occupied by solvent.

In the absence of steric effects *tert*-butyl groups on a metal-bound phosphorus atom should result in an increased electron density on the metal relative to phenyl groups and hence should facilitate oxidative addition. Thus with sterically undemanding substrates, including those which initially occupy only one coordination site, rates of reaction should be enhanced by the presence of *tert*-butyl groups. In the case of complexes of **3** and **4** the effect of the dimethylamino group seems to be to lower the electron density on the metal without exerting much steric influence. This leads to slow rates with the complex of **4** being more active. The results of the present investigation (Table V), in general, corroborate these ideas. Thus overall faster rates are obtained because of the presence of two phosphorus donors. However, the severe steric effects delineated above result in comparatively slower rates when the complex of **6** is used as a catalyst with chelating substrates. With simple olefins, the steric effects are minimized and the electronic effects maximized so that it is possible to get faster catalysis with the complex of **6**. However, it is difficult to account for the lack of reactivity of α-methylcinnamic acid.[32]

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada in the form of operating grants to W.R.C. and F.W.B.E. is gratefully acknowledged. We also thank Johnson-Matthey for the generous loan of rhodium salts.

Registry No. **6**, 84680-95-5; $[\mathbf{5}\cdot RhNBO]^+ClO_4^-$, 84680-96-6; $[\mathbf{6}\cdot RhNBO]^+ClO^-$, 84680-98-8; 1,1′-dilithioferrocene–bis(*N*,*N*,-*N′*,*N′*-tetramethylethylenediamine), 32677-77-3; chlorodi-*tert*-butylphosphine, 13716-10-4; 2-(acetylamino)-2-propenoic acid, 5429-56-1; 2-(acetylamino)-3-phenyl-2-propenoic acid, 5469-45-4; 2-methyl-3-phenyl-2-propenoic acid, 1199-77-5; 2-methylene-1,4-butanedioic acid, 97-65-4.

Supplementary Material Available: Tables of structure factor amplitudes (Table D), additional bond distances and angles (Table A), anisotropic thermal parameters (Table B), intramolecular H···H contacts (Table C), and positional and thermal parameters for hydrogen atoms (Table E) (33 pages). Ordering information is given on any current masthead page.

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(32) The methylcinnamic acid result is duplicated if the complex $[\widehat{P\ P})Rh(NBD)]^+ClO_4^-$, $\widehat{P\ P}$ = $(\eta^5\text{-}(C_6H_5)_2PC_5H_4)_2Ru$, is used as the catalyst precursor.[30]

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